NASA TT F-10,281

PRECAUTIONS IN USING THERMOBALANCES

C. Duval

Translation of "Précautions a prendre dans l'emploi
des thermobalances".
Analytica Chimica Acta, Vol.31, No.4, pp.301-314, 1964.

NOTICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON   SEPTEMBER 1966

PRECAUTIONS IN USING THERMOBALANCES* **/301

C.Duval

Based on data obtained in the pyrolysis of numerous in-
organic and organic substances in gravimetric analyses,
studies on volumetric standards, and solid-state reactions,
the differences in results obtained with various models of
thermobalances are discussed. Ten main causes of such dif-
ferences are given: type of apparatus, thermocouple, nature of
substance, weight of substance, rate of heating, nature of
ambient atmosphere, rate of flow of gas in the furnace, type
and form of crucible, sensitivity of recorder tracings, and
type and weight of residue. Standardization of these factors
is discussed and optimum characteristics of the apparatus
are described, giving preference to a balance with bifilar
suspension.

Thermogravimetry is now 60 years old. In 1903, Nernst in collaboration

with Riesenfeld (Bibl.1) combined an electric furnace with the microbalance

bearing his name and thus created the means for determining the mass of a given

body during heating. Later, Brill (Bibl.2) plotted the first thermolysis curve

for calcium carbonate, barium carbonate, and magnesium carbonate heated in a

continuous process to $1200°C$. Still later, in 1915, Honda (Bibl.3) suggested

---

** Numbers in the margin indicate pagination in the original foreign text.

the term "thermobalance" and a more recent book (Bibl.4) published in January 1961 lists more than 2400 papers on this particular question. Since then, 560 more such papers have been published.

At present (end of 1963), a total of 53 prototypes of thermobalances exist, of which 12 are actually on the market. These can be subdivided into three large groups: null balances, deflected-beam balances, and torsion balances; some are manual, others are automatic, mechanical, or electronic; a certain type produces a continuous recording of the weight loss as a function of temperature or time, while others use time or temperature derivatives and still others combine the curve of thermal weight with the curve of differential thermal analysis. In some models, the thermolysis process takes place in air at atmospheric pressure while in other models the same process takes place at 20 atm or else under 10^{-5} mm Hg or in a gas other than air; the rate of heating or cooling is almost always linear and varies between 0.5^{o}/min and 600°/hr; it is also possible to plot isotherm charts, operate with a glove box in the presence of radioactive products, etc.

Therefore, it would seem logical to compare the advantages and disadvantages of various thermobalances, their performance, their error limits, etc. However, we are not yet that far. Certain apparatus have been placed on the market too recently and their few users, at present, are content to merely accumulate the recordings. No price lists or catalogs are available for comparison purposes.

The Chevenard thermobalances, which were the first on the market and attracted the attention of several hundred buyers and a short time later had produced numerous good or bad recordings, naturally are the type for which the largest number of critical data exist.

2

However, until now we have been unable to obtain exactly the same data with four different commercial thermobalances, in studies on one and the same preparation of one and the same substance, heated at equal weight and at the same rate of heating; consequently, one can definitely state that thermogravimetry /302 is still in its infancy and that it just about is cutting its first teeth. The temperatures at which a given body decomposes or seems to decompose do not constitute a fixed point as is the case for the melting point of a substance. Ten parameters (or even possibly 12) seem absolutely necessary to consider here. We will make an attempt to do so, basing the studies on critical data communicated privately to the author.

Let us first recall that the initial work was performed with the purpose of a chemical analysis on inorganic chemical precipitates, to be subjected to gravimetry. Most of the results have been published since 1947 in Analytica Chimica Acta. The experiments always were made on 200 - 300 mg of moist precipitate, heated at maximum rate so as to approach as closely as possible the real operating mode of gravimetry, using aluminite crucibles. Thus it is impossible, as some authors have done, to compare the dissociation of a cubed calcite crystal with that of calcium carbonate obtained transitorily by the dissociation of oxalate. Similarly, it is difficult to find an analogy between the thermolysis of lanthanum oxalate, heated in vacuum or at atmospheric pressure; this would mean disregarding the law of mass action. It is possible only to compare comparable items. We will review the main factors by discussing them individually and, if necessary, indicate measures to remedy the defects. It will be demonstrated that some of the critical remarks are unjustified.

1. Brand of Thermobalance

Most of the commercial thermobalances are equipped with a knife edge (of

3

agate, steel, etc.); the only balances making use of a bifilar suspension are the Chevenard thermobalances. These latter are able to furnish the same curve after being in use for 25 years, even if the wires had been broken or replaced in the meantime. A prismatic knife edge is used up and, in turn, wears out its support; the edge softens or becomes rounded, which may have serious consequences for recordings lasting for several days, especially in a factory where certain vibrations are present. One can never be certain whether, during loading of the pan, the knife edge will retain its position. Only time will tell. However, the author recalls that in 1936 at Imphy, certain control recordings were made for periods of more than 40 days.

Other factors having to do with the design include: position of the inverted or uninverted furnace, location above or below the balance, position of the thermocouple, velocity of the air current, mode of recording, vibration dampers if they are used, all of which comprise factors to be discussed below. We believe that it is extremely difficult to compare balances of two different types, namely deflected-beam types or null balances, which are based on such widely differing principles and which are not subject to friction under exactly the same aspects; the same difficulty exists with spring balances which obey a different law and which, in general, do not operate in air at atmospheric pressure, or else differential balances which more or less completely suppress the influence of convection currents.

In general, a thermobalance is calibrated at low temperatures by placing it on a board or on a small platform attached to the crucible carrier of definite weight; this produces either a more or less deep break in the curve or the passage of a certain number of divisions through the field of view, or else the creation of an induced current. It seems extremely difficult to compare these

4

results. The calibration is not the same for all temperatures and for all /303

loads. The curve in Fig.1, referring to 300 mg calcium oxalate and plotted by

Newkirk (Bibl.5), shows that the displacement along the four plateaus remains

relatively constant in Chevenard thermobalances with pen recording at a velocity

of 300°/hr, if an overload of 20 mg is added. It is believed that this remains
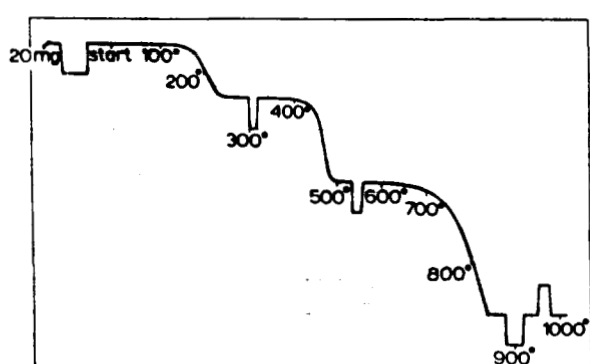

Fig.1 Effect of an Overload of 20 mg along the Plateaus
of the Curve for Calcium Oxalate Pyrolysis.

valid – other conditions being equal – so long as one does not exceed half of

the permitted load, i.e., 5 gm for the crucible and its content. If the time-

temperature curve is not a straight line (and this depends on the program de-

vices of the apparatus) within the range of $0 - 1200^o$, it is suggested – as done

by various authors (Papailhau, Erdey, and others) – to record the heating curve

on the same paper strip as the thermolysis curves. In the Chevenard-Joumier

system, a clock mechanism regulates this program. This naturally results in a

high regularity. In most of the other devices, the part in question is driven

by a synchronous motor, of which it is assumed that it will always be synchron-

ous which, however, was not the case in France during World War II.

2. Thermocouple

Four different points will be differentiated here: type, calibration,

5

position, and corrections. Until now, users of thermobalances have preferred

the platinum-platinum 10 or 20% rhodium system and nickel-chromium couples. The

selection depends on the cost price of the apparatus and on the heating range.

In the former case, the calibration curve is an open parabola up to 200°C and

then changes to a straight line. In certain thermobalances, the calibration is

done by the manufacturer, but in most cases the operator himself uses the boil-

ing point of water or aniline, the melting points of tin or lead, the boiling

point of sulfur, the melting point of antimony, sodium chloride, silver, or

gold. The cold junction is not always placed in melting ice but often in a

metal block which follows the temperature fluctuations of the part. To save

platinum, this "cold" junction is frequently placed quite close to the furnace

so that its characteristic temperature must be checked and noted during the

heating process in order to correct the figures read from the calibration curve,

toward either side. Such a correction is useful only for a few degrees and

becomes entirely illusory if the calibration had been made at 15°C while the /304

temperature of the thermocouple rises to 30°C. The calibration must be made

with the hot junction placed in a protecting silica tube which latter is halfway

submerged in the calibration substance without touching the walls. In the case

of gold, some metal can be saved by recording the breakdown temperature of a

wire surrounding the tube and traversed by an electric current while still in

the furnace. In the course of time, the chemical, mechanical, and electrical

properties of the junction and of the wires will change. A calibration is re-

quired from time to time - for example, every year - in the case of daily

measurements. In general, it is not the temperature of the substance which is

determined in a thermobalance but that of an air layer surrounding the crucible.

Of course, this is of no importance in the case of automatic dosing of the

substances as done by the author. In some models, the hot junction comes into contact with the crucible, as is the case in the "derivatograph". In deflected-beam balances, it is difficult to bury the hot junction in the product contained in the crucible. This is entirely possible in null balances, but these have the drawback of a possible alteration of the platinum by liberated products (hydrofluoric acid, arsenic, etc.) or by melts (potassium nitrate, chlorates, etc.).

It should also be mentioned that, if one wishes to place a programed furnace into a thermostat which previously had been exposed to continuous heating, it is suggested - because of the calorific inertia of the furnace - to stop the temperature rise to a few tens of degrees below the temperature one wishes to maintain.

3. Type of Substance

In our own publications since 1947 we have given general rules on the operating mode or at least on the principle of the method for obtaining heated precipitates. Even if a given substance was obtainable commercially in a fully prepared form, such as barium sulfate, we always prepared it ourselves and washed it in accordance with the principles of analytical chemistry. The origin of the minerals should be given each time because of variable impurities they might contain. In general, it is impossible to obtain the same curve for a product stored for years in the cabinets of a mineral collection and the same type mineral freshly extracted from the mine. In fact, such minerals in time will harden, lose moisture, liberate sulfuric gases, arsenic anhydride, etc. at room temperature. The thermal conductivity of the mineral will change and, because of the change in rate of heating, the initial decomposition temperature will generally rise. This is especially pronounced when the thermolysis curves

of a given mineral and of the synthetic product, for example of brucite and magnesia $Mg(OH)_2$, are plotted on the same diagram. The allotropic variants will yield non-superposable curves; this is specifically encountered with calcite, aragonite, and vaterite. The curves will also differ depending on whether a precipitate has matured, has been filtered after one hour, after 24 hours, or after one week. This is especially distinct in colloidal products and is readily explained. Similarly, a precipitate moistened by the washing fluids, such as obtained in routine analyses, will not give the same curve as a precipitate more or less partially dried in air. In the former case, it is possible to record the initial temperature of the dry-body plateau, which constitutes a practical problem; however, even here differences occur with different precipitants (which has an influence on the grain size and on their solvent retention). The phenomenon is quite obvious in the various variants of alumina, zirconia, /305 and beryllium hydroxide.

If the precipitate is large in volume, due to the amount of retained water, it is suggested to use low heating rates as indicated by Newkirk (Bibl.5). Thus, in treating the zinc and salicylaldoxime complex at a rate of 380°/hr, it is impossible to find a plateau for the complex. When dry, the same product will yield a plateau ranging from 25° to 285°C, in accordance with Rynasiewicz and Flagg (Bibl.6). A partially hydrated product (50%) shows a plateau of 135° to 190°C, in accordance with a heating rate of 300°/hr. An initially dry specimen which later had been moistened to 63% furnishes a plateau between 245° and 315°C.

The amount of water retained by the precipitate has an influence on the conductivity of the material, and the liberated vapor considerably changes the furnace atmosphere; in addition, it is generally known that any vaporization has a cooling effect.

8

Numerous researchers have investigated the grain size of the substance in question, in studies in which the fate of dry substances rather than the problems of analysis were of interest. The first of these authors [Saito (Bibl.7)] made comparative heatings with sulfidic ores and metallic sulfarsenides, whose grains were passed through screens of predetermined mesh. Naturally, the research by the above author was controlled by the operation of pyrite furnaces. The finer the grain the lower will be the initial decomposition temperature.

Vallet (Bibl.8) also studied the influence of the grain size, specifically of copper sulfate; in a paper written on my suggestion, Richer and Vallet (Bibl.9) compared the decomposition threshold of pure dry R.P. (783°) calcium carbonate in nitrogen at a rate of 150°/hr with the threshold of powdered calcite (802°C) and of calcite in the form of a cube weighing 352 mg (891°C). The latter crystal retains its form but becomes somewhat smaller in size since the process takes place in air. The authors gave no data on a precipitated and still moist calcium carbonate, which goes to their discredit since it is quite seldom that an analyst will be able to weigh a calcium carbonate precipitate in the form of a harmonious cube, in a nitrogen atmosphere.

4. Weight of the Substance

The weight of the substance (and thus its volume) has a considerable influence on the initial decomposition temperatures. In addition, if chelates formed from a metal and a difficultly combustible organic product are involved, the residual tar will disappear more rapidly the lower its weight, and the oxide plateau (or that of the final carbonate) will start at widely varying temperatures; this effect is especially pronounced with quinoline derivatives. For this reason, we allowed for a wide safety margin by heating the analytical

precipitates at a rapid rate and by using weights between 100 and 300 mg. This was never fully understood by other authors, specifically by Wendlandt. The heat of reaction, no matter whether it is positive or negative, will always change the difference between the temperature of the specimen and that of the furnace.

Newkirk (Bibl.5) mentioned that the method of differential thermal analysis is applicable here since this difference exists; it is quite significant that, in this technique, high heating rates are used (for example, 600°/hr) to emphasize the differential temperature.

Since, at this rate of heating, such a differential temperature may well extend to above 10°C, the kinetic constants calculated from the thermograms /306
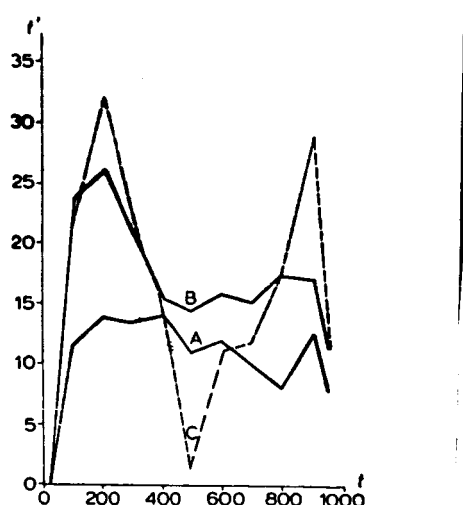

Fig.2 Deviation in Temperature due to the Sample;
Decomposition of Calcium Oxalate Monohydrate.
Rate of heating: 600°/hr. A = empty crucible; B = crucible +
+ 0.2 gm oxalate; C = crucible + 0.6 gm oxalate.

must be erroneous if the reaction is endothermal; however, if the reaction is exothermal, the effects have a mutually compensating tendency. In fact, the influence of the heat of reaction may be extremely great, as shown by the example of the oxidation of tungsten carbide in air [Newkirk (Bibl.10)]. The

10

thermograms show that the same reaction velocity was obtained with the thermobalance furnace kept constant at a temperature of 527°C or heated uniformly in a continuous manner. The effect is shown distinctly in Fig.2, provided that the differential temperature between the thermocouple t and that of the crucible t' had been measured directly for the decomposition of calcium oxalate monohydrate at the high heating rate of 600°/hr for two specimens of different size. The curve A for the crucible alone shows a deviation of 10° to 14° in the interval from 100° to 1000°C. When using a sample of 0.2 gm, the endothermal loss of water manifests itself in a deviation of 25 to 200°; the exothermal loss of carbon monoxide comes close to the difference observed with the crucible alone, but the deviation increases further during the endothermal loss of carbon dioxide. With a sample of 0.6 gm, these effects are cumulative and, at a single point, the temperature of the sample and that of the furnace will be almost the same.

5. Rate of Heating

Most of the present-day thermobalances are equipped with devices permitting a linear heating at rates ranging from 0.6° to 10°/min. It has been mentioned above that such a high heating rate will lead to frequently considerable variations in final and initial temperature of the plateaus; in addition, some of these may even disappear entirely or manifest themselves only in a discontinuity or inflection point. The case is especially clear in substances rich in /307 water of crystallization, such as the sulfates of the magnesium series. If one wishes to obtain one of these hydrates, the heating should be done as slowly as possible or the furnace should be placed into the thermostat on reaching the expected plateau.

Thus, Fruchart and Michel (Bibl.11), in heating nickel sulfate heptahydrate

at a rate of 0.6°/min were able to demonstrate hexahydrate, tetrahydrate, di-
hydrate, and monohydrate. At 2.5°/min, Demassieux and Malard (Bibl.12) only
found the monohydrate plateau. In turn, Newkirk (Bibl.5) proved the change in
the classical calcium oxalate monohydrate curve when passing from 300° to
150°/hr (shifting of the plateaus toward low temperatures). Figure 3 shows the
influence of the heating rate on the decomposition of a polystyrene sample, kept
in nitrogen, with the remaining fraction plotted as ordinates. Sabatier
(Bibl.13) observed a similar effect during the dehydration of mica. For samples
heated between 12° and 30°/hr, the threshold temperatures for a given weight range
from 735° to 815°C, i.e., a difference of 80°.
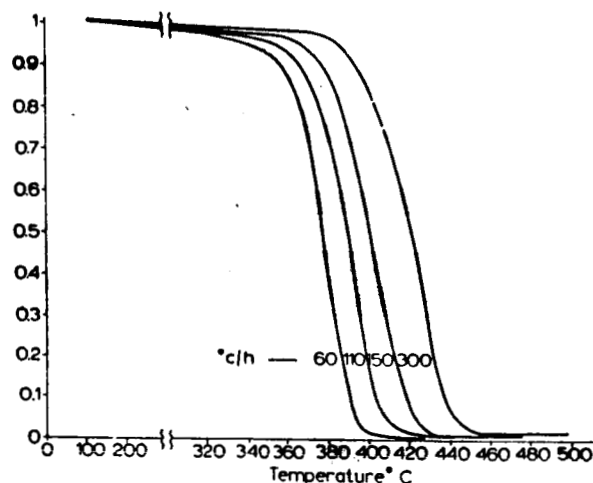

Fig.3 Pyrolysis of Polystyrene in Nitrogen, at
Various Heating Rates.

The effect of the heating rate is especially important if the thermogram
is to be used later for kinetic analyses.

6. Nature of the Ambient Atmosphere

This question has been studied by numerous authors after Saito (Bibl.7)
who used hydrogen, oxygen, nitrogen, sulfur dioxide, etc. The heated material

12

is not in equilibrium with the ambient atmosphere during decomposition but may be quite close to this equilibrium during recording of the plateaus. If the furnace atmosphere contains a gas liberated by the substance, a rise in initial and final temperature must be expected. Vallet (Bibl.8) observed the same effect when heating copper sulfate pentahydrate, while Vallet and Richer (Bibl.9) observed it in the dissociation of calcium carbonate in carbon dioxide. It must be expected that variable temperatures are encountered here since, although /308 the gases rapidly approach temperature equilibrium, the gas arriving in the cold state at the bottom or roof of the furnace must necessarily exert an influence on the gas liberated by the substance in the crucible. Since the vapor tension regulates the stability of the hydrates, Vallet was able to cause the copper sulfate trihydrate plateau to appear or disappear at will. Haladjian and Carpéni (Bibl.14) arbitrarily prevented dehydration of orthoboric acid, and produced or prevented the formation of the metaboric acid plateau, etc.

On heating calcium carbonate in carbon dioxide and then in nitrogen, Richer and Vallet (Bibl.9) found that the decomposition threshold is well-defined (900°C) in the first case and fairly well-defined (about 500°C) in nitrogen. This is not the same for the temperature at which the decomposition terminates, being between 914° and 1034°C in carbon dioxide and between 683° and 891°C in nitrogen.

Fortunately, in an analysis in which a thin layer of material (moistened at the beginning) is heated at atmospheric pressure, the differences are not quite that large. A gas or a vapor, liberated by the substance, may have an influence on the slope of the curve; when heating salts or organic chelates, specifically carbon monoxide is partially able to reduce the residue. After its elimination, the air current (or oxygen) usually causes a rise in the curve.

The reduction is especially well-defined in the case of Streng uranium salt, divalent copper which passes into the metallic state, or cuprous oxide.

We made use of the heating of gypsum in a water vapor atmosphere and of deuterogypsum in a heavy water atmosphere for preparing both light and heavy plasters (Bibl.15).

Making use of the Chevenard thermobalance, Newkirk (Bibl.5) applied a heating rate of 300°/hr for heating calcium oxalate precipitated at the same weight, but hermetically sealing the top of the furnace and then ventilating through a hole of 7 mm diameter. The two curves coincide, except at high temperatures, on the calcium oxide plateau. The differences increase when using sodium carbonate heated first in air and then in carbon dioxide. At 300°/hr, the decomposition threshold is $850^\circ C$ in air but is not yet reached at $1050^\circ C$ in carbon dioxide (250 ml/min). Sodium tungstate, at 28 molecules of water, furnishes widely differing curves, at least up to $175^\circ C$, depending on the humidity of the ambient air. In a more recent investigation, Garn and Kessler (Bibl.16), operating in a self-induced atmosphere, studied the thermal decomposition of cadmium carbonate, ammonium carbonate, lead carbonate, manganese carbonate, and dehydrated cobalt oxalate, using open or closed vessels.

7. Velocity of the Gas Stream

This factor is of prime importance, which is easily understood when considering that the nature of the gas surrounding the crucible plays a significant role. Most thermobalance furnaces are of the open type and thus contain a mixture of air, introduced gas, and liberated gas or vapor. It is obvious that, depending on the velocity of the gas stream, the furnace atmosphere will change causing a modification in the length and position of the plateaus. In one of

14

his first experiments, Vallet (Bibl.8) heated 400 mg of identical copper sulfate
pentahydrate samples at 42°/hr, in a dry air stream whose output was 6.6 ltr/hr
for the one sample and 34.0 ltr/hr in the other (Fig.4). Appearance of the tri-
hydrate was not influenced by an increase in output. This will lead to a sort
of translation of the mass-temperature curve, parallel to the temperature axis
in the direction of decreasing values. This shift is less pronounced for the /309
curve segment referring to the dehydration of the pentahydrate than for the
curve referring to the trihydrate and is weaker for the latter than for the
terminal segment referring to the dehydration of the monohydrate. Saito
(Bibl.7) obtained similar results, for example with manganese dioxide heated in
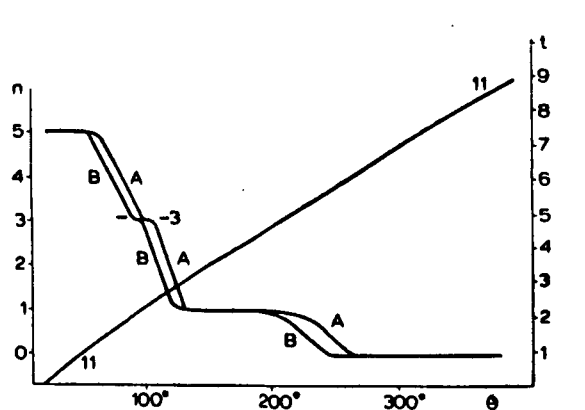hydrogen.

Fig.4 Influence of the Volume of Dry Air on the
Dehydration of Copper Sulfate Pentahydrate.

In the preceding Section, we referred to the furnace ventilation which is
a relatively important factor. Actually, in thermobalances with furnaces open
at the top, i.e., into which the crucible is "plunged", the circulation of the
gases takes place primarily by convection and the crucible is subject to variable
pressures that change its real weight and show in a rather regular rise in the
curve with increasing temperature. In inverted furnaces, of the type used in
the Chevenard thermobalance, two or three holes are made in the cover cap which

15

can be either open or closed; this naturally changes the velocity of the air

stream and has an influence on the more or less rapid renewal of the atmosphere

and the more or less rapid dissipation of the liberated gases. In our experi-

ments from 1936 to 1946, we always obtained a perfectly horizontal straight line

(in other words, a curve returning to its initial position after one turn of the

drum) when heating, to a temperature of 1050° C, a substance which neither loses

nor gains weight during this interval, such as a gold or platinum crucible. We

used this fact and this entirely reliable control to develop a method of auto-

matic gravimetry. We also observed an oxidation previous to the explosion of

the oxidizing materials. Since that time, various authors have published curves

that disagree with ours, despite the fact that all conditions of heating rate

were the same; these authors specifically noted an increase in weight of samples

for which we obtained a constant value. Because of this disagreement, re-

searchers at the General Electric Co. (Schenectady, N.Y.), Simons, Newkirk, and

Aliferis (Bibl.17) plotted a correction curve after heating objects of molyb-

denum, platinum, porcelain, etc.; they estimated an increase in the hot air

(Fig.5) to 1037° C may lead to a rise of the curve (straight line above 200° C)

corresponding to 5 mg per 200 mg. In addition, Mielenz, Schieltz, and King

(Bibl.18) obtained a correction curve of S-shape (Fig.6), using the same

thermobalance with a sag between 700° and 800° C; the apparent weight gain was

again of the order of 5 mg in 1.5 gm samples, up to a temperature of 1000° C. It

seemed to us that the deviations produced when heating a constant-weight sub-

stance were due to the design of the metal cap closing the furnace at the top.

This cap ordinarily is provided with a hole for accommodating the silica tube

of the thermocouple and with two vents of 2 mm diameter that ordinarily are

blocked. In our original thermobalance models, the cap had holes of different

16

diameters (having been used for preliminary experiments) which could be removed
at will. In addition, these caps fitted much less tightly into the upper collar
of the furnace than in more recent models (incidentally, the diameter of the
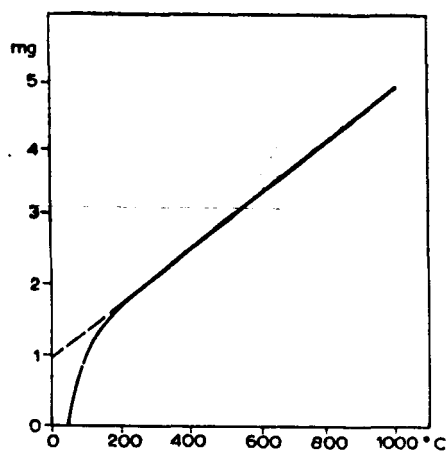cap changes after repeated heatings over a period of about 10 years).

Fig.5 General Plot of Apparent
Weight as a Function of Tempera-
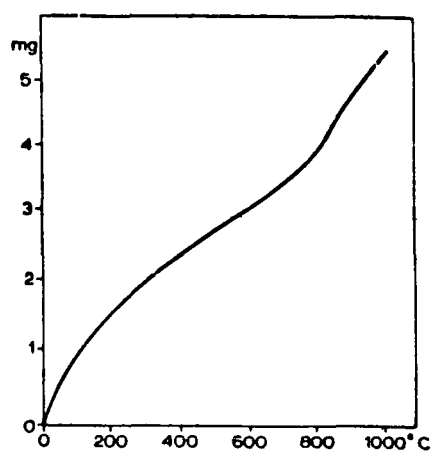ture, according to Simons, Newkirk,
and Aliferis.

Fig.6 Correction of Pressure for
Heating Cycle of the Thermo-
balance.

After this, we equipped our apparatus with metal caps, having a central
hole and six smaller holes (Fig.7) arranged symmetrically and closeable at will.
Depending on the number of open holes, it is possible, using the same heated
body and obeying the same law, to obtain either a rising straight line (case in
which all holes are closed or opened in an asymmetric fashion) or else a hori-
zontal line (in other words returning exactly to the origin after one rotation
of the drum, no matter what the starting point of the drum had been) or, finally,
a drooping straight line. This means that it has been entirely pure chance that
our own apparatus had been equipped with an adequate cap.

We next thought of providing the central hole with a progressive obturation
system, similar to that used in iris diaphragms of cameras; however, this great-

ly complicates the affair and does not always operate properly, specifically at high temperatures. We found it simpler (Bibl.19) to provide the central hole with rings of various thicknesses which could be adapted in the fashion of stove rings or the rings of a water bath (Fig.8). We selected crucibles having the same upper and lower diameter; before any pyrolysis, we adjusted the diameter <u>/311</u> of that ring which, together with the heated crucible, yields a straight line, i.e., a line parallel to the temperature axis.
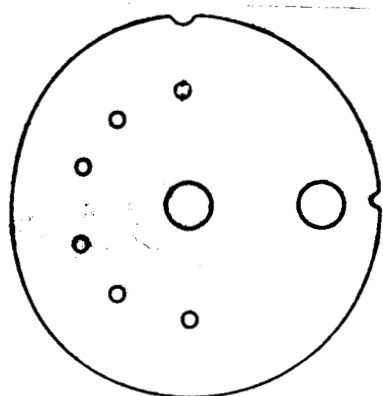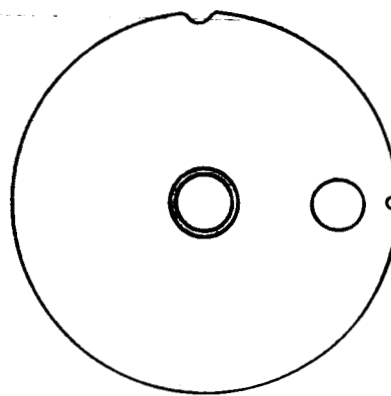

Fig.7 Furnace Cap with Six Symmetric-   Fig.8 The Same Cap, with Central
ally Arranged Holes.   Hole.

Only relatively few data are available on the fate of curves obtained with a substance heated at a pressure below or above atmospheric. The problem is highly complex and changes further depending on whether or not the gas or liberated vapors are dissipated. It seems logical to assume that, in dissipating the gaseous products, it would be easier to keep the pressure constant and to lower the decomposition threshold. It could also be imagined that the influence of convection currents can be reduced by decreasing the pressure. This was found by Eyraud and Goton (Bibl.20); however, as soon as a pressure of 1 mm Hg was reached, a new and just as important error source appeared, produced by collision of molecules on the sample. Eyraud was able to compensate this drawback by

18

using a balance of his own design.

Below, we give a few values of the radiometric pressure, expressed in mg, exerted on the specimen holders of about 12 mm diameter, suspended in a quartz tube of 17 mm inside diameter and heated in a vertical Chevenard furnace of type CT_2, open at both ends. The following values were recorded at a pressure of 0.1 mm Hg and a temperature of $500^{\circ}C$:

Placement of the Boat	Pressure
Upper third of furnace	+2.2 mg
Center of furnace	-1.1 mg
Lower third of furnace	-5.0 mg

It was also found that, during a continuous temperature rise, with the boat at a constant position, the radiometric pressure does not always vary in the same sense; it may return to zero and then even change sign.

At $800^{\circ}C$, with the boat in constant position and the heating law being the same, the radiometric pressure reaches the following values, as a function of air pressure:

Air pressure	5	3	1	1/10	1/1000 mm
Radiometric pressure	0.0	0.5	1.0	2.2	3.3 mg

For objects of more or less identical bulk and similar position inside the furnace, the results vary widely. At $600^{\circ}C$ and a pressure of 1/1000 mm, the following were noted:

Object Used	Radiometric Pressure
Quartz boat	+1.5 mg
Porcelain capsule	+2.9 mg
Solid quartz bar	+1.0 mg

The phenomenon thus is due to the asymmetry of the pressure exerted on the

recipients by molecule collisions which either may come from the cold portions
of the enclosure or from the hot portions. A simple remedial solution consists
in placing the boat into an intermediary enclosure, rendered quasi-isothermal
by its reduced form. A small opening is left in the upper portion, to permit
passage of the suspension wires. The efficiency of such a device was quite
satisfactory; this device must be used as soon as the pressure drops below
3 mm Hg.

8. Type and Form of Crucible

Until now, crucibles in the shape of a truncated cone of high or low form,
regular cones, hemispherical capsules, square plated of 1 cm side with raised
borders, or crucibles with a bottom in the form of a bottleneck were used for
accommodating the heated substance. The crucible materials ranged from platinum,
gold, silver, tungsten, and nickel to silica, porcelain, glass, aluminite,
thoria, zirconia, and steatite. Although no truly systematic tests were made
with a single variable, it can be stated that a difference exists in the decom-
position thresholds when using a metal crucible which is a good heat conductor
or a crucible made of oxides or silicates. The differences may range from 5°
to 10°.

The shape itself plays an important role, even at atmospheric pressure, in
view of the fact that, since the walls are heated more intensely than the
center, one must allow for the characteristic conductivity of the substance
itself and the rate of diffusion of the gases leaking through the grains. The
solution of using a plate or a thin layer seems best while that of a high
crucible is the poorest solution. Some substances cause projections or swell
and expand excessively, but in some cases, their use is unavoidable. Garn and

Kessler (Bibl.16) made a detailed study of these factors, in heating experiments with lead carbonate and hydrated cobalt oxalate. Newkirk and Aliferis (Bibl.21) investigated the behavior of dry sodium carbonate in gold, platinum, alumina, and porcelain crucibles. Apparently, the influence of the type of metal is negligible. Conversely, placement or removal of a cover on the crucibles has a considerable effect. This involves a previously investigated factor, namely, the velocity of the gas stream. It is generally known that water will boil more rapidly on a gas flame, when contained in a pot with a cover. During pyrolysis, dissipation of the gases is inhibited so that the curve plateaus assume an elongated form. It is even possible to promote the formation of such plateaus. As early as 1936, we found that, in the case of ammonium magnesium phosphate, no discontinuity appears between the separation of water and ammonia in an open crucible; when the same crucible is provided with a cover, a small plateau or at least a break occurs in the curve as soon as no more ammonia is liberated and as soon as the $MgPO_4H$ phosphate is pure.

Another factor of some importance is the erosion of the crucible, i.e., /313 a solid-state reaction between the glaze or the material of the crucible itself with the liberated gases. It is obvious that this will lead to a parasite weight loss. An excellent example was given by Newkirk and Aliferis (Bibl.21) in the pyrolysis of sodium carbonate in a quartz crucible, in which erosion started above $500°C$.

It should be mentioned that, when heating molybdic anhydride in a porcelain crucible, the bottom of the crucible will turn bluish-green but without a change in weight or, more accurately, without weight variations exceeding 0.1 mg per 4 gm.

9. Sharpness of the Tracing

By photographic recording on coated paper, tracings (although only faintly visible) of 0.1 mm thickness are obtained; using a stylus with triangular platinum tip, a relatively nonabsorbent paper, and glycerol ink, it is difficult to go below thicknesses of 0.5 mm. It is obvious that this thickness is of great importance for computations in the case of minor weight fluctuations. In certain apparatus, Chevenard was able to plot the curve by means of a series of closely adjacent points, produced by a needle that periodically contacted the paper. However, we believe that this factor is not quite as important as all the others. Primarily, the factor has an influence on the sensitivity similar to the effect of the clock movement, the meshing of the gears, the inertia of photoelectric cells, and the unforeseen variations in electric current strength.

10. Type and Weight of the Residue

Generally, it is this final plateau that is used for calculating the molecular weights, so as to determine, from the ordinates of the other plateaus, the nature of the initial substance and of the intermediate products. This presupposes that the final product has a known composition and that it does not absorb water during the cooling process, before having been weighed on an analytical balance for control. However, numerous metal oxides become carbonated at the end of the process and nevertheless yield a fairly horizontal plateau. We also mentioned a possible combination with the substance of the inside crucible walls. Spot analyses on the residue are thus necessary if the calculations do not yield a logical solution. It would be useful to terminate

this particular paper with a calculation for the error occurring in thermo-
balances. Unfortunately, we did not have the necessary materials available.
Until now, we only have the partial results on the Chevenard thermobalance at
our disposition; in addition, the ten prime factors enumerated above have not
all been taken into consideration. However, we wish to refer to the extremely
useful exploratory experiments by Simons, Newkirk, and Aliferis (Bibl.17) with
a pen recorder, and the experiments by Claisse, East, and Abcsque (Bibl.22) as
well as by Mielenz, Schieltz, and King (Bibl.18) with a photographic-recording
thermobalance.

11. Summary

Based on 25 years of experience in the pyrolysis of several thousands of
inorganic and organic substances, specifically for gravimetric analyses,
studies of volumetric standards, and investigations on solid-state reactions,
the author uses his own personal experience in an attempt to explain the   /314
discrepancies reported by users of various models of thermobalances. These
discrepancies are traced to ten principal causes: brand of apparatus, type of
thermocouple, nature of the substance involved, weight of this substance, rate
of heating, nature of the atmosphere surrounding the crucible, rate of flow of
the gas in the furnace, type and form of the crucible, fineness of the recorder
trace, and nature and weight of the residue.

BIBLIOGRAPHY

1. Nernst, W. and Riesenfeld, E.H.: Ber., Vol.36, p.2086, 1903.
2. Brill, O.: Z. Anorg. Chem., Vol.45, p.275, 1905.
3. Honda, K.: Sci. Rept. Tohoku Univ., Vol.4, p.97, 1915.

4. Duval, C.: Inorganic Thermogravimetric Analysis. Second Edition, Elsevier Publ. Co., Amsterdam, 1963.

5. Newkirk, A.E.: Anal. Chem., Vol.32, p.1558, 1960.

6. Rynasiewicz, J. and Flagg, J.F.: Anal. Chem., Vol.26, p.1506, 1954.

7. Saito, H.: Sci. Rept. Tohoku Univ., Vol.16, p.1, 1927.

8. Vallet, P.: Compt. Rend., Vol.198, p.1860, 1934; Thesis, Paris, May 23, 1936; Ann. Chim., Vol.7, p.298, 1937.

9. Richer, A. and Vallet, P.: Bull. Soc. Chim. France, p.148, 1953; Compt. Rend., Vol.249, p.680, 1959.

10. Newkirk, A.E.: J. Am. Chem. Soc., Vol.77, p.452, 1955.

11. Fruchart, R. and Michel, A.: Compt. Rend., Vol.246, p.1222, 1958.

12. Demassieux, N. and Malard, C.: Compt. Rend., Vol.245, p.1514, 1957.

13. Sabatier, G.: J. Chim. Phys., Vol.52, p.60, 1955.

14. Haladjian, J. and Carpéni, J.: Bull. Soc. Chim. France, p.1679, 1956.

15. Duval, C., Lecomte, J., and Pain, C.: Compt. Rend., Vol.237, p.238, 1953.

16. Garn, P.D. and Kessler, J.E.: Anal. Chem., Vol.32, p.1900, 1960.

17. Simons, E.L., Newkirk, A.E., and Aliferis, I.: General Electric Company Report, No.56-RL-1522.

18. Mielenz, R.C., Schieltz, N.C., and King, M.E.: Proc. 2nd Natl. Conf. Clays and Clay Minerals, Missouri, Oct.13–17, 1953. Publication 327 of The National Academy of Sciences, p.285, 1954.

19. Duval, C.: Mikrochim. Acta, p.705, 1958.

20. Eyraud, C. and Goton, R.: Bull. Soc. Chim. France, p.1009, 1953.

21. Newkirk, E. and Aliferis, I.: Phys. Chem. Research, No.405, General Electric Company; Anal. Chem., Vol.30, p.982, 1958.

22. Claisse, F., East, F., and Abesque, F.: The Use of the Thermobalance in

Analytical Chemistry. Dept. of Mines, Province of Quebec, Canada, 1954.